

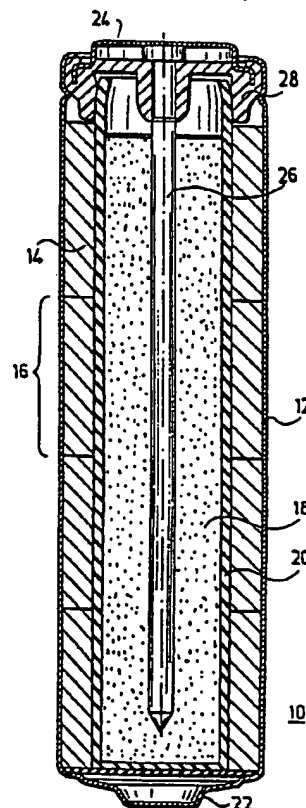
PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : H01M 4/50, 4/62, 6/04	A1	(11) International Publication Number: WO 93/12551 (43) International Publication Date: 24 June 1993 (24.06.93)
(21) International Application Number: PCT/CA92/00553 (22) International Filing Date: 21 December 1992 (21.12.92) (30) Priority data: 4047/91 19 December 1991 (19.12.91) HU (71) Applicant: BATTERY TECHNOLOGIES INC. [CA/CA]; 30 Pollard Street, Richmond Hill, Ontario L4B 1C3 (CA). (72) Inventors: TAUCHER, Waltraud ; KORDESCH, Karl ; Stremayrgasse 16, A-8010 Graz (AT). DANIEL-IVAD, Josef ; 54 Old Hill Street, Richmond Hill, Ontario L4C 9T9 (CA). (74) Agent: HEWSON, Donald, E.; 2145 Dunwin Drive, Suite 13, Mississauga, Ontario L5L 4J9 (CA).		(81) Designated States: AU, BB, BG, BR, CA, CS, FI, JP, KP, KR, LK, MG, MN, MW, NO, PL, RO, RU, SD, Euro- pean patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: CATHODES FOR ZINC MANGANESE DIOXIDE CELLS HAVING BARIUM ADDITIVES**(57) Abstract**

A cathode structure for alkaline manganese dioxide-zinc primary or rechargeable cells with improved capacity that comprise manganese dioxide active material, a conductive powder and an additive material uniformly mixed and pressed to form a porous body, wherein the additive is a barium compound which is at least 3 % mass of the solid components. The preferred additive is barium oxide, barium hydroxide or barium sulphate. The invention relates also to alkaline manganese dioxide-zinc primary or rechargeable cells, wherein the cathode structure is employed.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

CATHODES FOR ZINC MANGANESE DIOXIDE CELLS HAVING BARIUM ADDITIVES

FIELD OF THE INVENTION:

The invention relates to improvements relating to alkaline manganese dioxide-zinc cells and more particularly to a cathode structure for alkaline manganese dioxide-zinc cells with improved capacity, which comprises as solid components manganese dioxide active material, a conductive powder and an additive material. The solid components are uniformly mixed and pressed to form a porous body and the pores thereof are filled with electrolyte when the cathode structure is used in a cell.

BACKGROUND OF THE INVENTION:

Manganese dioxide is a widely used cathode material for alkaline primary batteries. Its rechargeability in alkaline solutions makes this material also attractive for rechargeable battery systems. Electrolytic manganese dioxide exhibits a limited rechargeability as disclosed by K. Kordesch et al, in *Electrochim. Acta*, 26, 1495 (1981) corresponding to the depth of discharge and this fact decreases the available capacity in practice.

The optimization of the cathode structure has long been the objective of various development activity. U.S. patent 4,384,029 issued to K. Kordesch et al deals with the properties of the manganese dioxide cathode material and with the composition of the cathode mix. The cathode structure is made of a mixture of electrolytic manganese dioxide powder as active material and graphite powder or colloidal graphite, and the mix is kept together either by a binding agent and/or by the application of pressure. The graphite has the task of improving conductivity. The addition of further materials like polymers or co-polymers of styrene, butadiene, acrylonitrile, urea, formaldehyde, vinyl alcohol, or epoxy resins was suggested. These materials called generally as "additives" had the purpose of improving the structure and of decreasing the swelling of the cathode material during cycling. A requirement generally imposed

to such additives was that they had to be wettable by the electrolyte. Experience had shown that despite the presence of these additives in the cathode the cell voltage after a number of cycles decreased:

In U.S. patent 4,929,520 issued to K. Kordesch et al the use of conducting washers was suggested between contacting blocks of the cathode body, whereby the internal resistance of the cell was decreased to a significant extent.

A further concern connected with the design of the cathode structure is the problem of hetaerolite formation which reduces the active manganese dioxide mass during the cycle life of the cell. This phenomenon has been discussed widely in the literature, a recent approach can be found in the paper of E. Preisler: Voltage Measurements on Alkaline Primary Cells During Discharge and Recovery (Progress in Batteries & Solar Cells. Vol. 9, 1990, IBA York Meeting pp 21-34). During the discharge the zincate concentration increases in the electrolyte by dissolution of the zinc electrode and zincate migrate to the cathode. The zinc ions penetrate to the active zone of the cathode and react with the reduced manganese oxide to form hetaerolite. During cycling the presence of hetaerolites has the following effects:

- it cannot participate any more in the cycling process, i.e. the amount of the active cathode mass is reduced (up to about 30% of all active material), whereby the cell capacity decreases;
- it expands mechanically and this tends to destroy the cathode structure.

To overcome the expansion tendency, means like perforated solid metal cages or increased amount of binding agents were used which further reduced the available space for active material and decreased conductivity.

The drawbacks of hetaerolite formation are not limited to rechargeable cells, similar drawbacks appear in primary cells, when they are discharged in intermittent time intervals.

It is the primary objective of the present invention to provide appropriate additive materials by which the above drawbacks can at

least partially be eliminated.

A further objective of the invention is the use of additive materials which lessen the cell voltage reduction during cycling of rechargeable alkaline manganese dioxide-zinc cells.

It has been found according to the present invention that the use of specified barium compounds as additive materials i.e. barium oxide, barium hydroxide or barium sulphate can well satisfy all the above objectives if added to the solid components of the cathode in an amount of at least 3% mass or preferably 5% to 25% mass.

In a preferable embodiment barium hydroxide is used as additive that includes 8 moles of water of crystallization.

In the alkaline manganese dioxide-zinc cell, in the presence of potassium hydroxide electrolyte barium oxide tends to form barium hydroxide with the electrolyte.

The use of barium sulphate as additive material in about the same concentration as barium oxide or hydroxide provides similar advantages in cell performance, however, this choice is preferred, since barium sulphate is environmentally indifferent and commercially available at reasonable costs.

Measurements with these suggested additive materials have shown that the cell voltage during cycling, under any predetermined load, changes substantially less than that of cells without the additives.

The presence of barium compounds in the close vicinity of the active cathode material may reduce the access of zinc ions to the manganese dioxide, therefore, hetaerolite formation is substantially slowed down.

The suggested additive materials are all wettable by the electrolyte and their particle size is very small. This circumstance increases the utilization of the available manganese dioxide mass and reduces the internal cell resistance of cycled cells. These additive materials can be regarded therefore as efficient pore modifiers.

The beneficial effects of the presence of the suggested barium compounds as additive materials will be more apparent in view of test data collected from different kinds of alkaline manganese dioxide cells.

In the following examples the test and control cells have identical design and structure with the only different that control cells do not contain any barium compound as additive.

It will be apparent from the examples that the cell capacity per cycle and the cumulative capacity both increase rapidly when the amount of the additive material is about 3% of total mass. The performance does not improve further if the amount of the additive exceeds about 25% of total mass since in case of larger additive quantities the effect of decrease of the active mass becomes more dominant.

BRIEF DESCRIPTION OF THE DRAWINGS:

The invention will now be described in connection with preferable embodiments thereof, wherein reference will be made to the accompanying drawings. In the drawing:

Figure 1 shows a cross section of an alkaline manganese dioxide-zinc rechargeable cell;

Figures 2 and 3 show the discharge capacities and cumulative capacities of cells with cathodes comprising 0%, 10% and 15% of total mass barium sulphate;

Figures 4 and 5 are similar to Figures 2 and 3, they show discharge capacity and cumulative capacity curves for cells with 0%, 10% and 15% of total mass barium hydroxide with 9 molecular water;

Figures 6 and 7 show similar discharge capacity and cumulative capacity curves for cells with 0%, 10% and 15% of total mass barium oxide;

Figure 8 shows the cumulative capacity curves of tested and standard AA cells as a function of cycle number; and

Figures 9 and 10 show cell capacity versus cycle number curves for test and standard AA cells.

DESCRIPTION OF THE PREFERRED EMBODIMENTS:

Figure 1 shows the cross-sectional elevation view of an alkaline manganese dioxide zinc rechargeable cell 10. The cell comprises the

following main units: a steel can 12 defining a cylindrical inner space, a manganese dioxide cathode 14 formed by a plurality of hollow cylindrical pellets 16 pressed in the can, a zinc anode 18 made of an anode gel and arranged in the hollow interior of the cathode 14, and a cylindrical separator 20 separating the anode 18 from the cathode 14. The ionic conductivity between the anode and the cathode is provided by the presence of potassium hydroxide electrolyte added into the cell in a predetermined quantity.

The can 12 is closed at the bottom and it has a central circular tip 22 serving as positive terminal. The upper end of the can 12 is hermetically sealed by a cell closure assembly which comprises a negative cap 24 formed from a thin metal sheet, a current collector nail 26 attached to the negative cap 24 and penetrating deeply in the anode gel to provide electrical contact with the anode, and a plastic top 28 providing a sealing gasket between the negative cap 24 and the can 12, electrically insulating the negative cap 24 from the can 12 and separating gas spaces formed beyond the cathode and anode structures, respectively. For understanding the present invention there is no need for a more detailed structural description of the cell.

To demonstrate the effectivity of the present invention the impact of different barium compounds on the cell performance was tested.

The first test series was carried out with "C" type cells referred also to as LR-14 cells (IEEE standard designation). The cathodes 14 were formed from a mixture of manganese dioxide and graphite powder pressed to form the pellets 16 and the anode consisted of a zinc gel mixture. The measurements were carried out on respective test and standard cells which differed only in the composition of the cathode mixture. The cathodes of the test cells comprised the below specified barium compounds which replaced corresponding masses of manganese dioxide.

The test and standard cells were charged and discharged periodically by means of a computer controlled testing arrangement which provided for the accurate reading and storage of test data (corresponding data for the cell voltage, time and charge/discharge

currents). All the cells were subjected to a testing program for about 40 days which included repetitive periods of charging with a constant 1.72 volt taper charger during 20 hours and of discharging with a 3.9 ohm load until the cell voltage dropped to 0.9 V. The current and voltage data were recorded every minute and the charge/discharge capacity was calculated automatically from the recorded data.

The product of the average discharge current and the discharge time in each cycle corresponds to the cell capacity for the cycle concerned. The cumulative capacity after a given cycle number is the sum of the capacities in all previous cycles.

Table 1 summarizes the cumulative capacity values for the standard and tested cell after 20 and 40 cycles.

Table 1
Cumulative capacities of LR 14 cells

compound	(%)*	after 20 cycles Ah	increase (%) vs. standard	after 40 cycles Ah	increase (%) vs. standard
BaO	10	49.3	50.3	81.2	55.0
Ba(OH) ₂ ·8H ₂ O	15	52.0	58.5	86.3	64.7
BaSO ₄	15	51.2	56.0	80.9	54.4
Standard	-	32.8	-	52.4	-

* percentage quantity of dry powder mix

Figures 2 and 3 show the discharge capacities and cumulative capacities of cells with cathodes that have 0%, 10% and 15% mass barium sulphate in the dry powder mix. The 0% curves show the performance of a standard cell.

Figures 4 and 5 are similar to Figures 2 and 3, they show discharge capacity and cumulative capacity curves for cells with 0%, 10% and 15% of total mass barium hydroxide with 8 moles crystal water. Figures 6 and 7 show similar discharge capacity and cumulative capacity curves for further cells with 0%, 10% and 15% of total mass barium oxide. Here the barium oxide forms barium

hydroxide with the water in the electrolyte.

This test series has demonstrated that in case of "C" size cells a quantity of 10% to 15% of total mass barium compound leads to substantial increase in cumulative capacity.

A further test series with a slightly different design of LR 14 "C" type cells was carried out, in which the dry mix of the cathode of the test cell comprised 7% mass barium sulphate and this constituted the only difference compared to the standard cell. The cumulative capacity results of this series are summarized in Table 2.

Table 2
Cumulative capacity of LR 14 cells with 7% BaSO₄
versus standard cell

cycle number	standard cell (Ah)	test cell (Ah)	increase (%)
5	14.8	16.4	11.2
10	23.6	27.4	15.9
15	30.9	36.2	17.1
20	37.3	44.1	18.1
25	43.0	51.3	19.4
30	48.2	58.4	21.1
35	53.3	65.1	22.2
40	57.8	71.0	23.0

A further test series was made with rechargeable alkaline manganese dioxide cells of AA size (LR 6 size according to IEEE standard) to establish the optimum amount of barium salt addition and to demonstrate the cell behaviour under different load conditions.

The test and standard cells differed in the cathode composition, in the test cell 5%, 10% and 15% mass barium sulphate was added at the cost of manganese dioxide. The anodes comprised mercury free zinc anode gel. The preparation of the standard and test cells occurred the same day. 20 cells of each group were manufactured and respective 3 cells were tested with 4 and 10 ohm discharge load at room temperature. 30 cycles were performed under computer controlled cycling conditions (cut-off voltage 0.9 V, 15 hours charge to 1.72 V) and the average cumulative capacities were calculated.

Table 3 contains the percentual changes in the cumulative capacity values of test cells relative to that of standard cells.

Table 3
LR 6 cells after 30 cycles

BaSO ₄ (%)	load 4 ohm cum. capacity %	load 10 ohm cum. capacity %
0	100	100
5	115	117
10	96	125
15	90	141

Figure 8 shows the cumulative capacity curves of the tested and the standard cells as a function of cycle number. The cells were loaded till a cut-off voltage of .9 V and charged with an 1.72 V charger through 15 hours. The ambient temperature was 22°C.

In case of other type test cells with 5% mass barium oxide in the cathode mix the cell capacity versus cycle number curves are shown in Figures 9 and 10. The test results with standard cells are also shown.

It can be seen from Table 3 and from Figures 8 to 10 both for LR 6 cells, that the presence of the barium compounds in the cathode brings about a larger improvement at medium and lower loads (i.e. if the load is 10 ohm than in case of high load represented by the 4 ohm).

In case of LR6 (AA size) cells the optimum percentage of barium salt is lower than in case of C size cells.

A further improvement caused by the presence of the barium sulphate and barium hydroxide lies in the increase of cycle life of the cell. For example conventional alkaline manganese dioxide LR 6 cells were tested on shallow cycling, and the standard cell gave on average 300 cycles, while the cells of similar design but comprising the barium compounds in the cathode gave on average more than 600 cycles.

From the point of view of manufacturing costs and environmental protection the use of barium sulphate is preferred. The barium sulphate is an inexpensive, commercially available powder, insoluble in water and is environmentally safe.

While the main advantages of the present invention appear in connection with rechargeable cells, the use of the suggested barium compounds in primary cells is also justifiable, since it reduces hetaerolite formation, thus increases the effective cell capacity. This increase becomes apparent mainly during intermittent use.

WHAT IS CLAIMED IS:

1. A cathode structure for alkaline manganese dioxide-zinc cells with improved capacity, comprising a manganese dioxide active material, a conductive powder and an additive material uniformly mixed and pressed to form a porous body, characterized in that said additive is a barium compound pre-sent in said body in an amount of at least 3% of total mass, said barium compound is selected from a group consisting of barium oxide, barium hydroxide and barium sulphate.
2. The cathode structure as claimed in claim 1, wherein said amount is between about 3% and 25% of total mass.
3. The cathode structure as claimed in claim 1, wherein said additive is barium hydroxide that may include water of crystallization.
4. The cathode structure as claimed in claim 3, wherein said barium hydroxide comprises eight molecules of water of crystallization.
5. The cathode structure as claimed in claim 1, wherein said barium compound is barium oxide.
6. The cathode structure as claimed in claim 1, wherein said barium compound is barium oxide, at least a portion of which forms barium hydroxide (BaOH) when mixed with an alkaline electrolyte.
7. The cathode structure as claimed in claim 1, wherein said barium compound is barium sulphate.
8. An alkaline manganese dioxide-zinc cell comprising a manganese dioxide cathode, a zinc anode, a separator between said anode and cathode an electrolyte, wherein said cathode comprises as solid components manganese dioxide active material, a conductive powder and an additive material, said solid components are uniformly mixed and pressed to form a porous body filled with said electrolyte,

characterized in that said additive is a barium compound constituting at least 3% of total mass of said solid components and being selected from a group consisting of barium oxide, barium hydroxide and barium sulphate.

9. The cell as claimed in claim 8, wherein said barium compound constitutes between about 3% and 25% of total mass of said solid components.

10. The cell as claimed in claim 8, wherein said additive is barium hydroxide that may include water of crystallization.

11. The cell structure as claimed in claim 10, wherein said barium hydroxide comprises eight molecules of water of crystallization.

12. The cell structure as claimed in claim 8, wherein said barium compound is barium oxide.

13. The cell structure as claimed in claim 8, wherein said barium compound is barium oxide, at least a portion of which forms barium hydroxide (BaOH) when mixed with said electrolyte.

14. The cell as claimed in claim 8, wherein said barium compound is barium oxide forming barium hydroxide with said electrolyte.

15. The cell as claimed in claim 8, wherein said barium compound is barium sulphate.

16. The cell as claimed in claim 8, characterized by being a primary cell.

17. The cell as claimed in claim 8, characterized by being a rechargeable cell.

18. The cell as claimed in claim 8, characterized by having a cylindrical design.

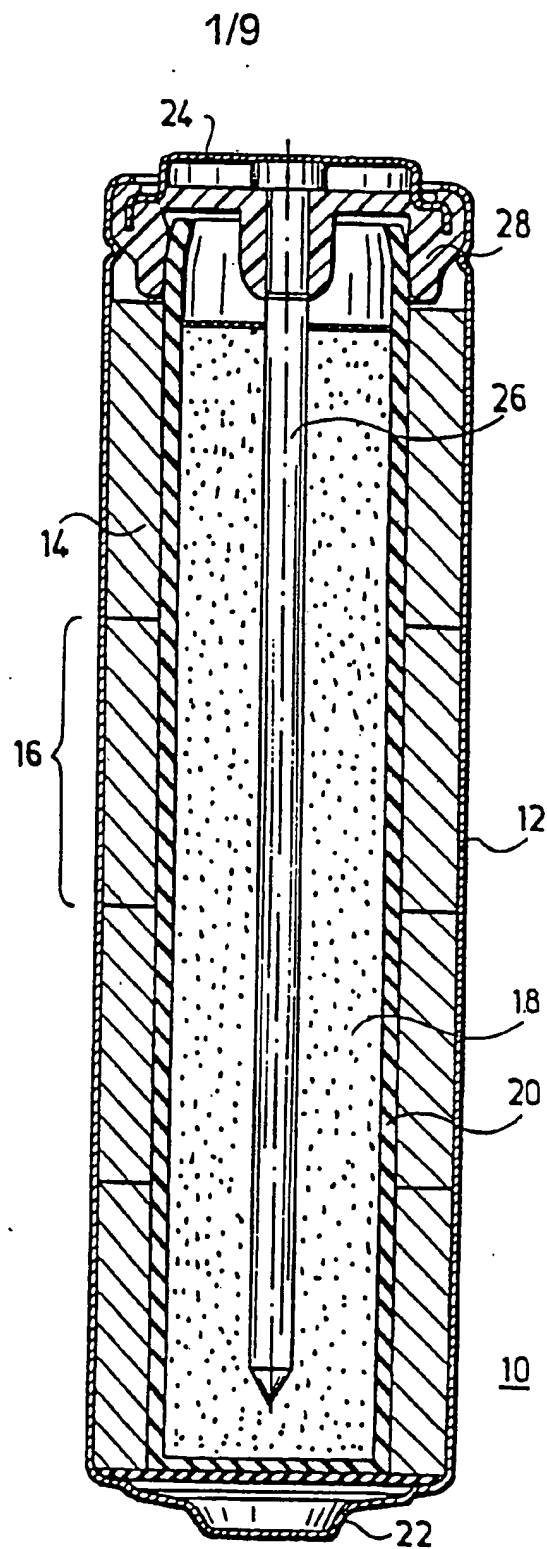


Fig. 1

2/9

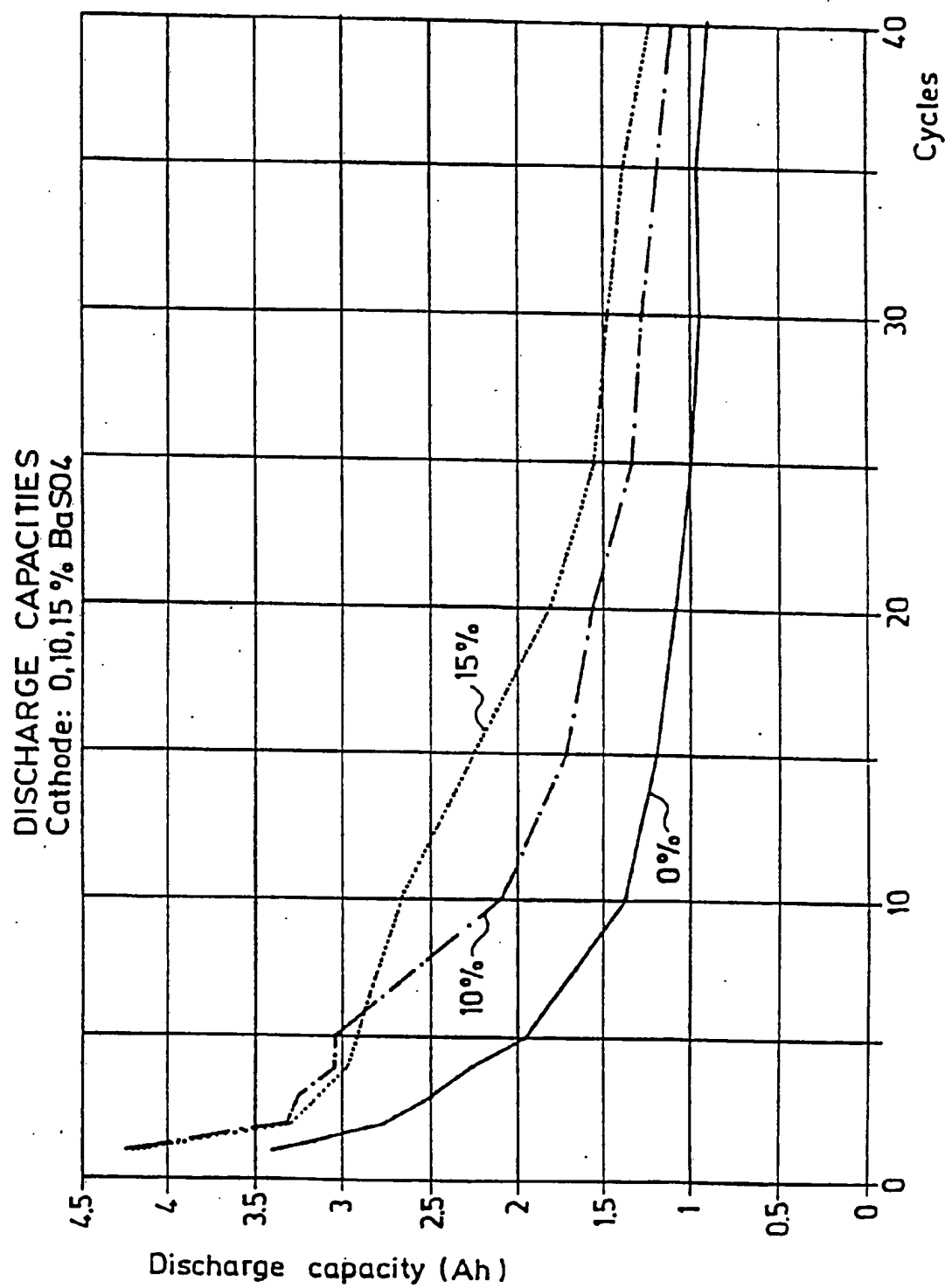


Fig. 2

3/9

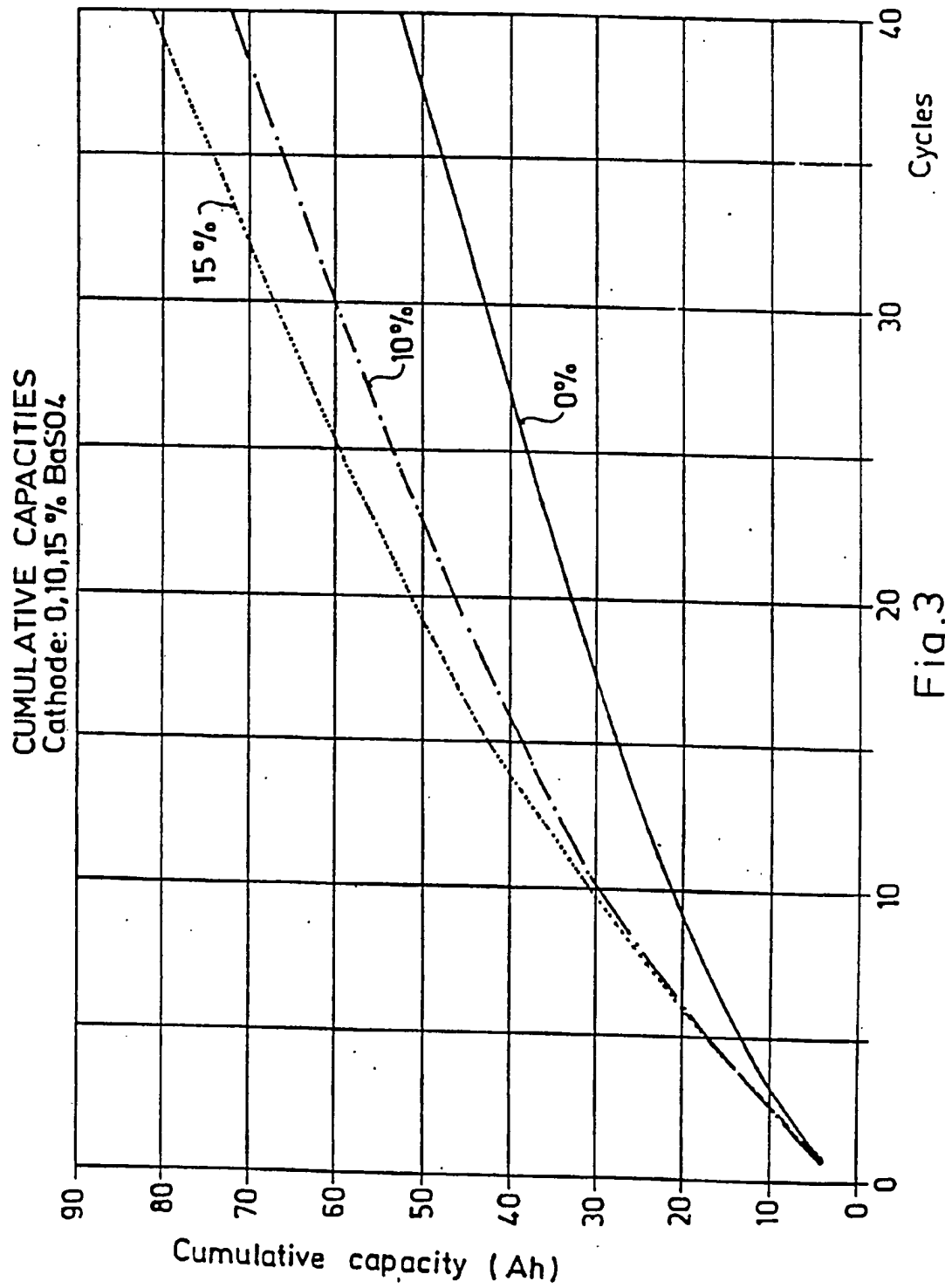


Fig.3

4/9

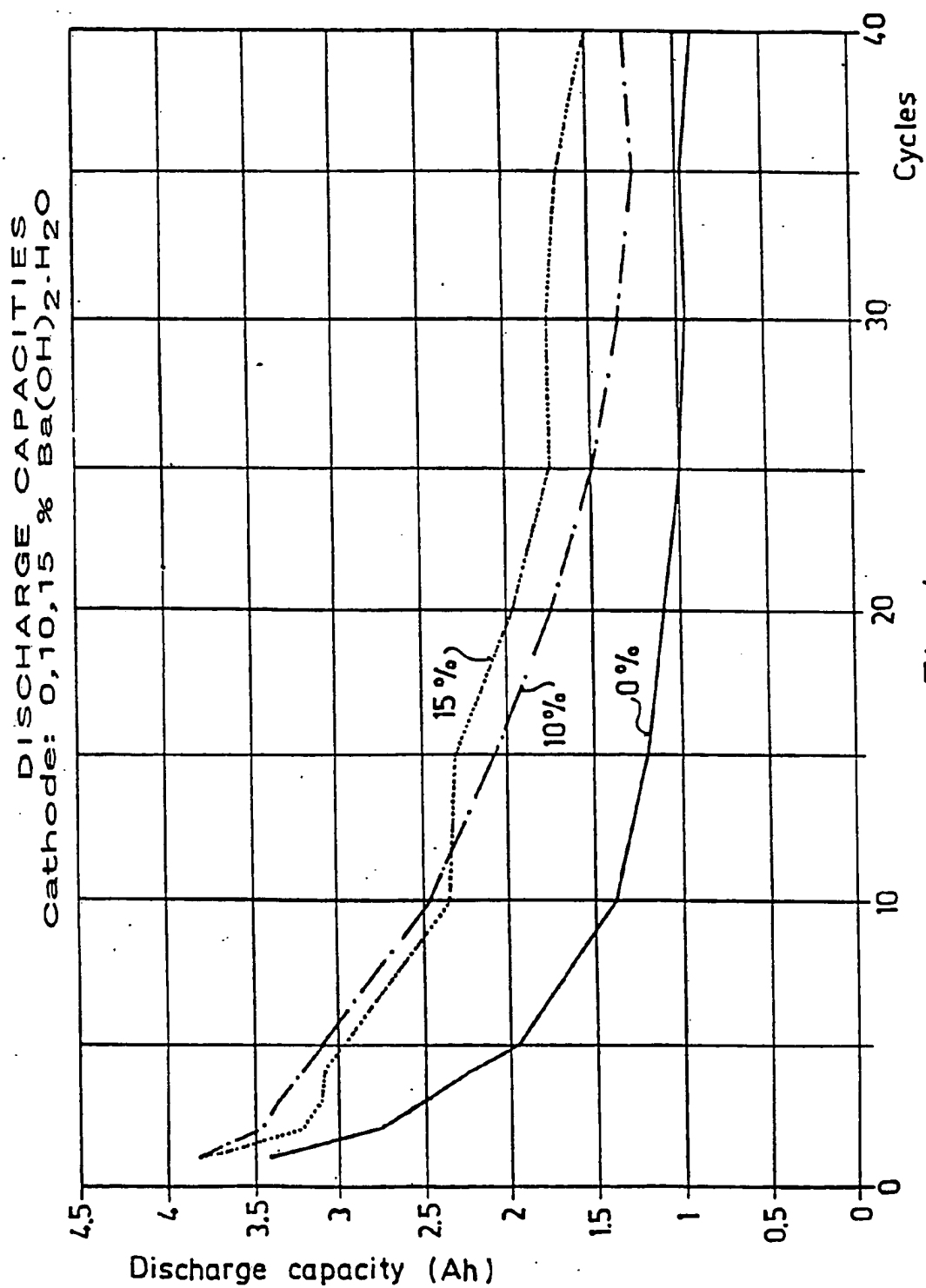


Fig. 4

5/9

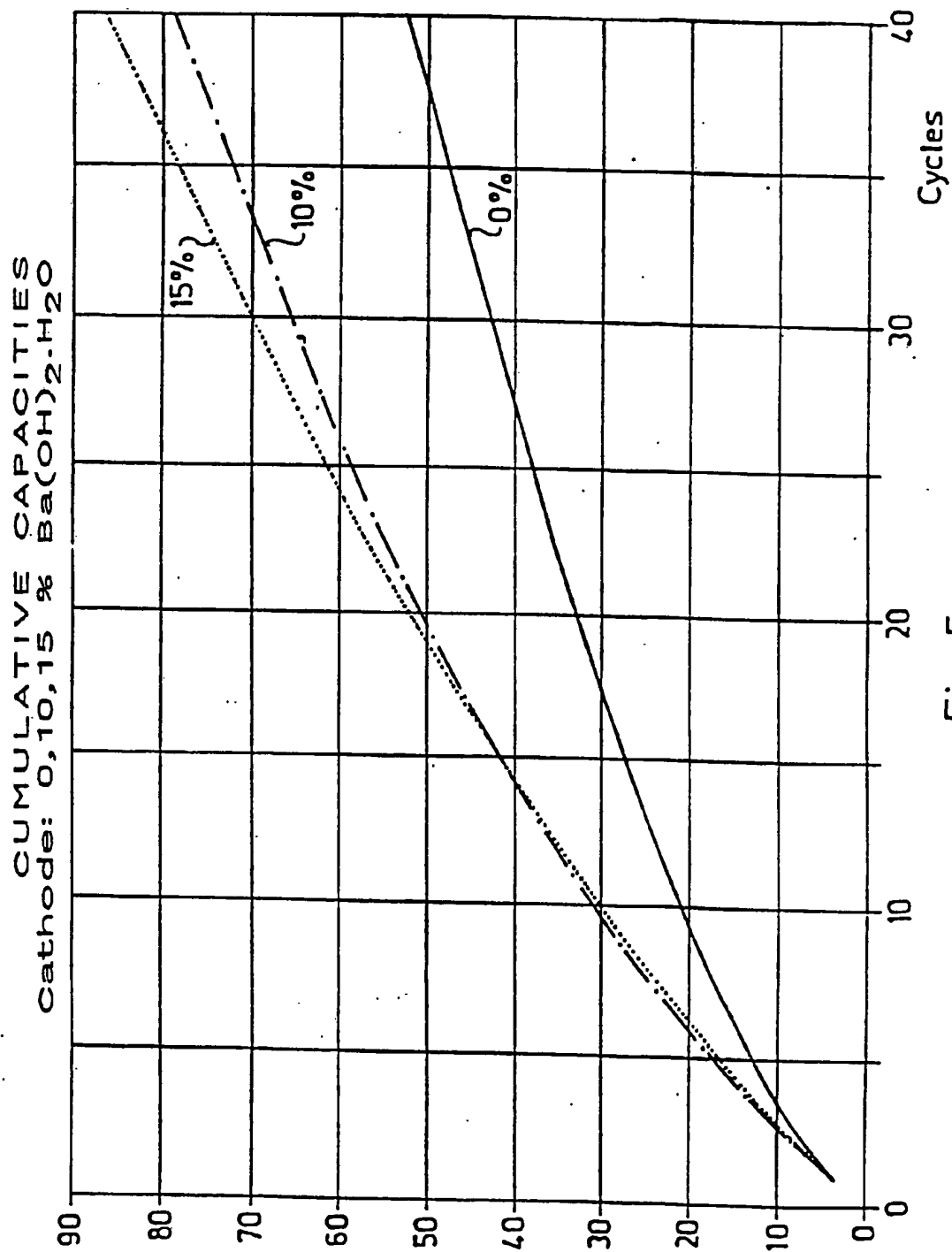


Fig. 5

6/9

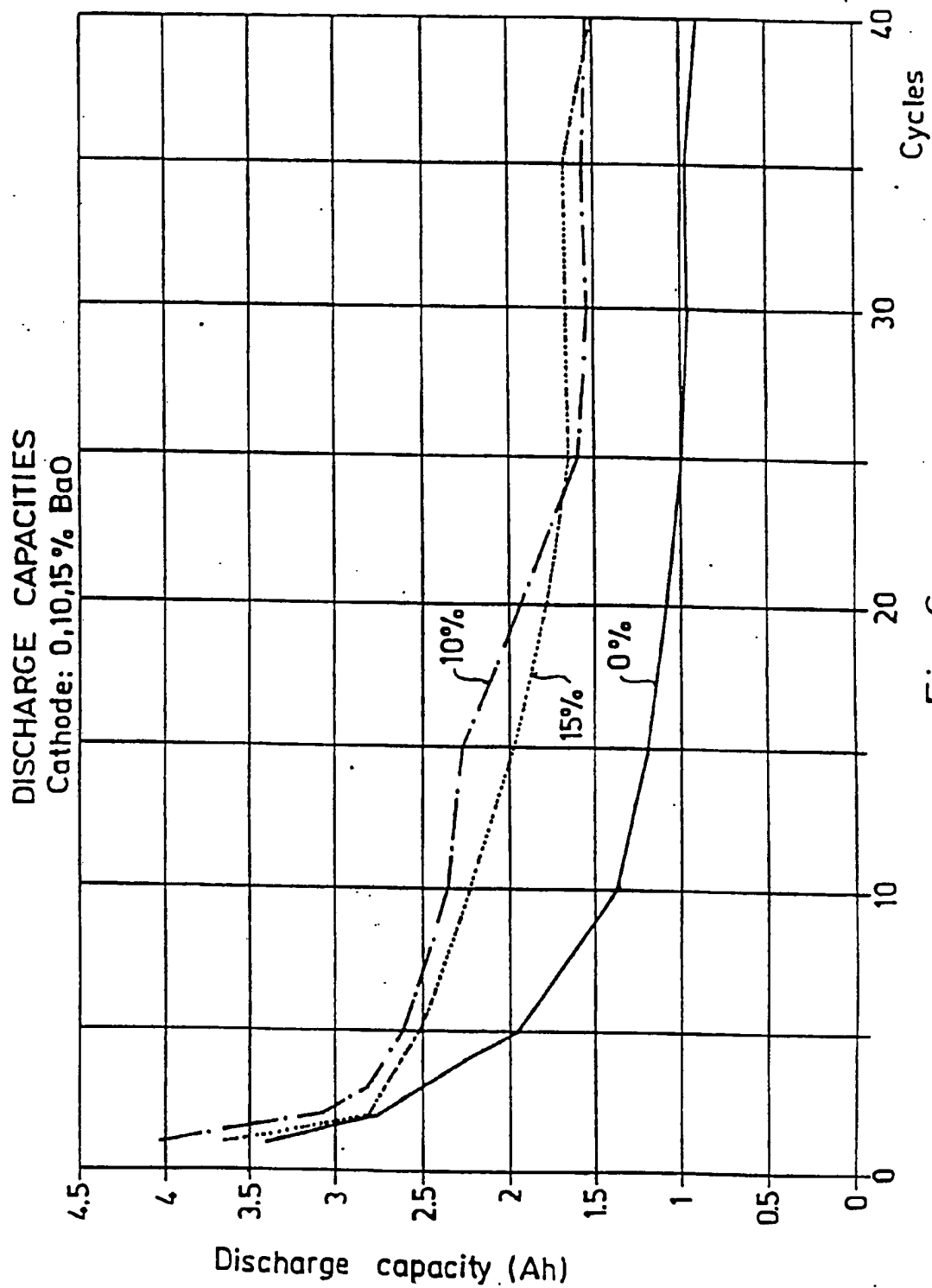


Fig.6

7/9

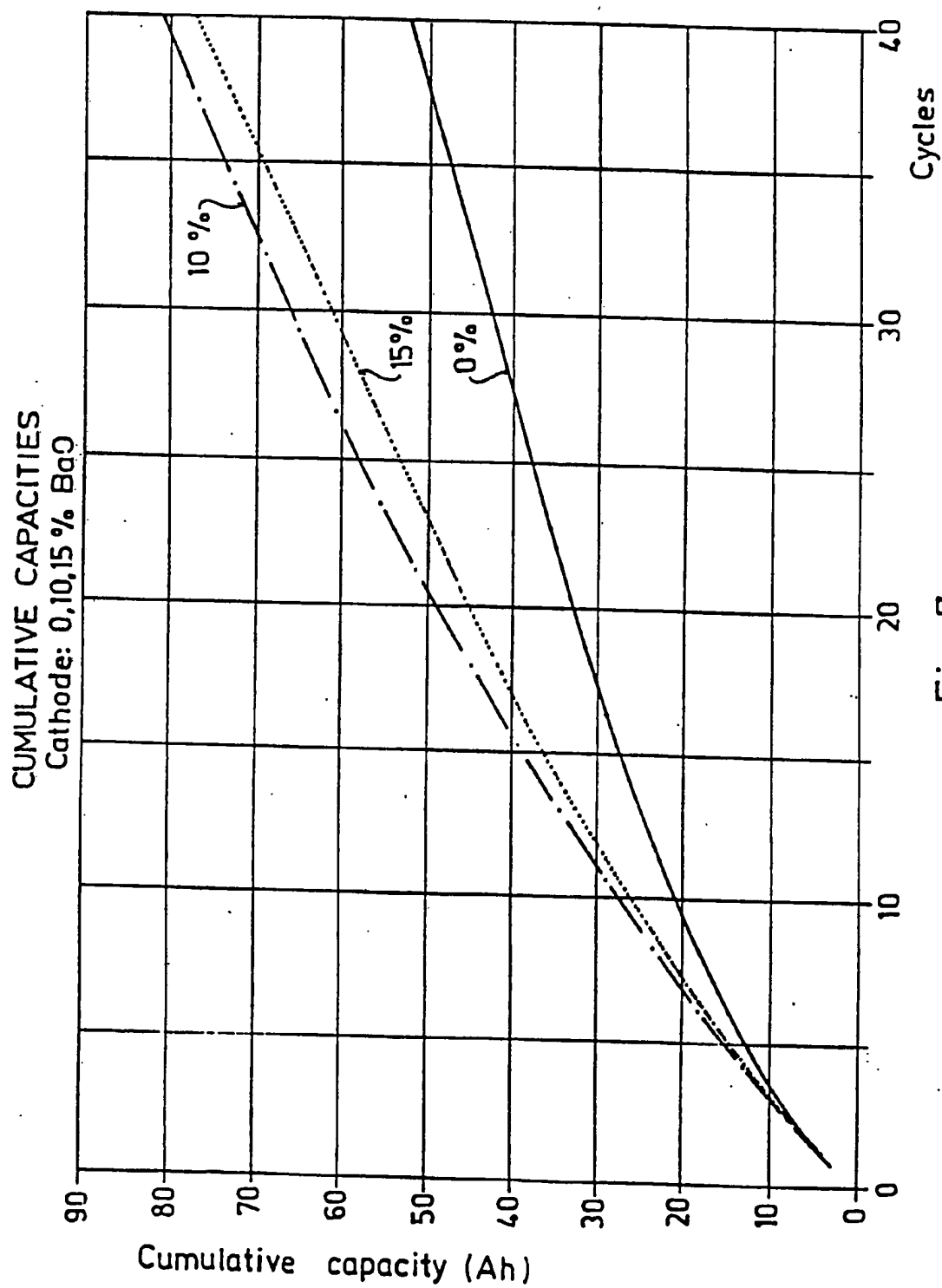


Fig.7

8/9

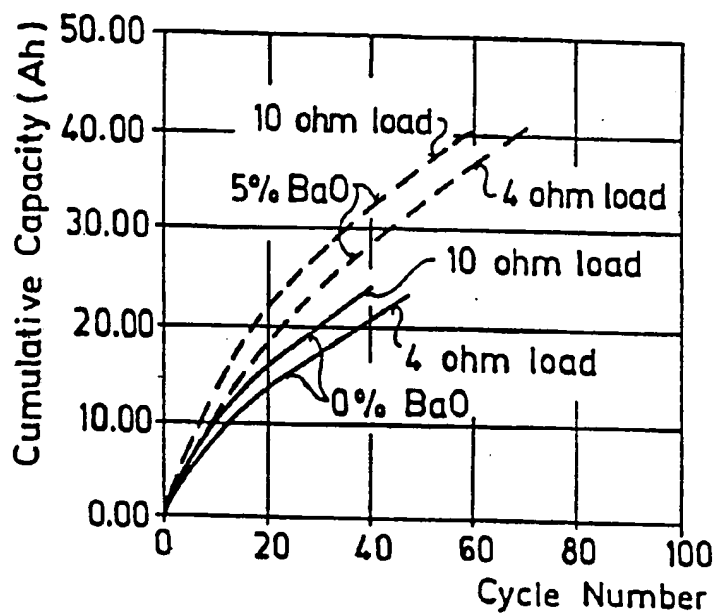


Fig.8

9/9

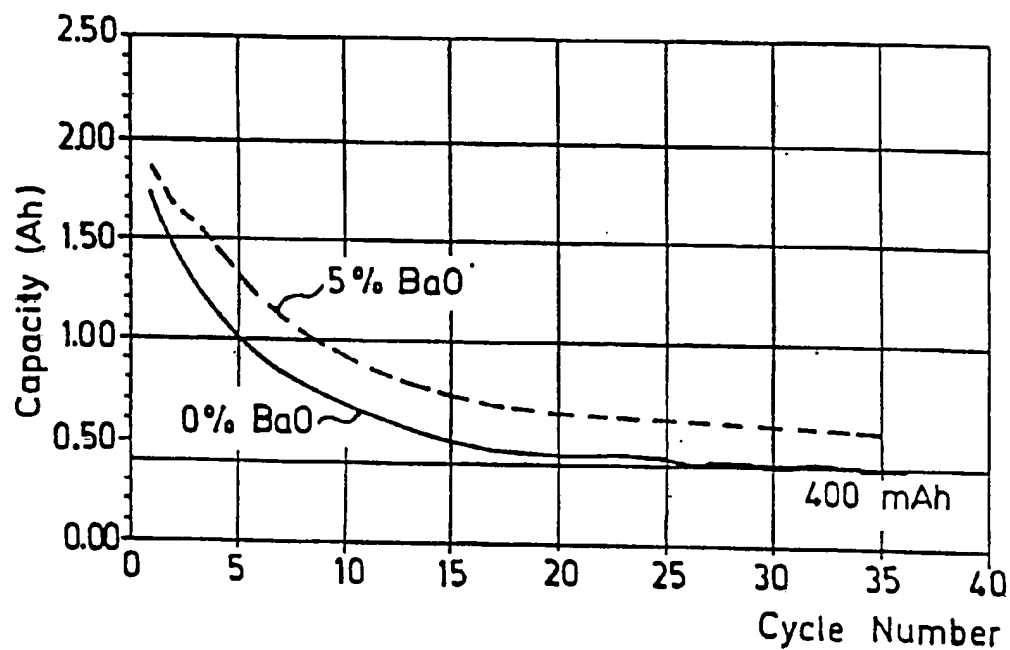


Fig.9

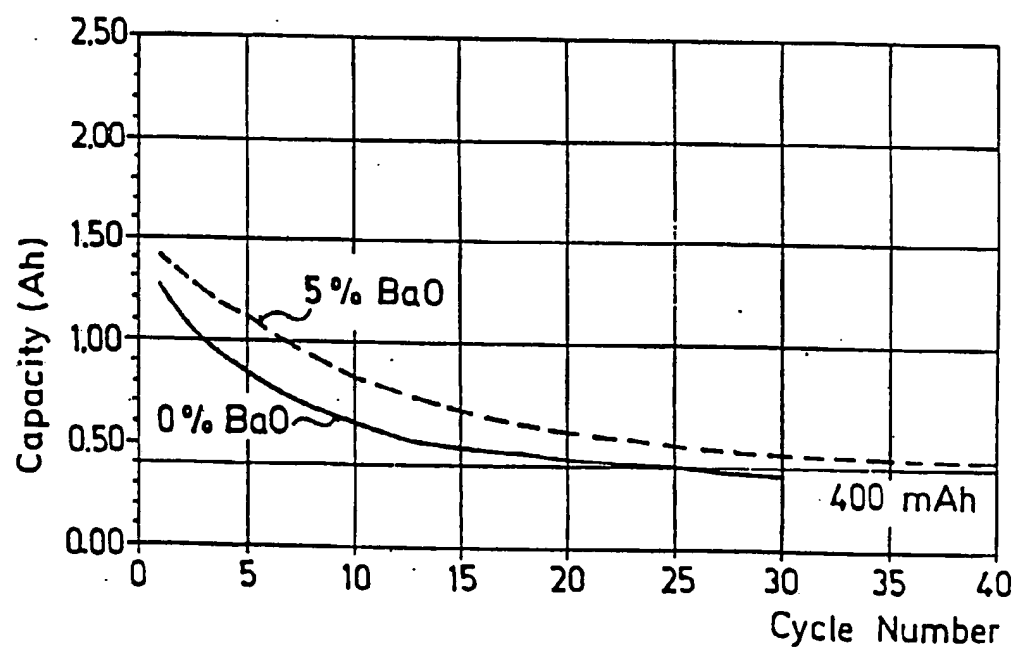


Fig.10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA 92/00553

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: H01M 4/50, H01M 4/62, H01M 6/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2, 0033853 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.), 19 August 1981 (19.08.81), page 6, line 30 - page 7, line 22 --	1,2,5,8,9, 12,16,17
X	EP, A1, 0110344 (UNION CARBIDE CORPORATION), 13 June 1984 (13.06.84), page 4, line 20 - page 5, line 33 --	1,2,8,9,16, 17
X	Patent Abstracts of Japan, Vol 9, No 53, E-301, abstract of JP, A, 59-194356 (TOSHIBA DENCHI K.K.), 5 November 1984 (05.11.84) --	1,7,8,15,16

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

23 March 1993

13.04.93

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. JI 651 epo nl,
Fax: (+31-70) 340-2016

Authorized officer

Ulla Granlund

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA 92/00553

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4384029 (KARL KORDESCH ET AL), 17 May 1983 (17.05.83), column 1, line 31 - line 63 -----	1-17

SA 8141

INTERNATIONAL SEARCH REPORT
Information on patent family members

26/02/93

International application No.

PCT/CA 92/00553

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0033853	19/08/81	JP-C- 1475639	18/01/89
		JP-A- 56103864	19/08/81
		JP-B- 63024301	20/05/88
		US-A- 4336315	22/06/82
EP-A1- 0110344	13/06/84	JP-A- 59112573	29/06/84
US-A- 4384029	17/05/83	DE-A,C- 3026065	04/02/82
		JP-A- 57049173	20/03/82